

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 53/02, 33/06, B05D 7/02	A1	(11) International Publication Number: WO 97/00913 (43) International Publication Date: 9 January 1997 (09.01.97)
(21) International Application Number: PCT/US96/06197 (22) International Filing Date: 2 May 1996 (02.05.96) (30) Priority Data: 08/493,633 22 June 1995 (22.06.95) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: GROVES, James, D.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: GWIN, Doreen, S., L. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	(81) Designated States: AU, BR, CA, CN, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: ACRYLATE-CONTAINING POLYMER BLENDS (57) Abstract A polymer blend comprising (a) a modified block copolymer comprising (i) a polystyrene block and (ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene block being modified to contain an average of one or more carboxyl groups; and (b) a polymer comprising a polymerization reaction product (i) at least one acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive, (ii) at least one monomer having carboxylic acid functionality which is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b); and (iii) a titanate selected from the group consisting of (ethanol,2,2',2"-nitrioltris-titanium(4+) salt); titanium bis(ethyl-3-oxobutanolato-O ¹ O ³)bis2-propanolato; a reaction product of tetraalkyltitanate with a β -diketone and an alkanolamine; and tetrabutyltitanate (1-butanol,titanium(4+) salt).		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

5

ACRYLATE-CONTAINING POLYMER BLENDS

Background of the Invention

10 Field of the Invention

This invention relates to polymer blends useful, e.g., as adhesives, primers, inks, and paints.

Description of the Background Art

15 Low surface energy substrates such as polyethylene, polypropylene, and other polyolefins are characterized as having critical surface tensions of wetting of about 35 dynes/cm or less. Such surfaces are generally unreceptive to inks, paints, and adhesives due to their poor wettability. There is a need to improve adhesion to such surfaces, as well as to high energy surfaces.

20

Summary of the Invention

The present invention relates to a blend comprising (a) a modified block copolymer comprising (i) a polystyrene block and (ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene
25 block being modified to contain an average of one or more carboxyl groups; (b) a polymer comprising a polymerization reaction product of two or more mono-ethylenically unsaturated monomers in which (i) at least one of the monomers is an acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive and (ii) at least one of the monomers has carboxylic acid
30 functionality and is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b); polymer (b) does not comprise a nitrogen-containing monomer.

The invention also relates to a method of priming a substrate comprising applying to the substrate a blend comprising (a) a modified block copolymer comprising (i) a polystyrene block and (ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene block being
5 modified to contain an average of one or more carboxyl groups; (b) a polymer comprising a polymerization reaction product of two or more mono-ethylenically unsaturated monomers in which (i) at least one of the monomers is an acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive and (ii) at least one of the monomers has carboxylic acid functionality and
10 is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b); polymer (b) does not comprise a nitrogen-containing monomer.

In particular, the present invention also relates to a method of enhancing adhesion between a substrate and an adhesive (for example, a pressure-sensitive
15 adhesive, a thermosetting adhesive, a thermoplastic adhesive) comprising the steps of priming said substrate by applying to said substrate a blend comprising (a) a modified block copolymer comprising (i) a polystyrene block and (ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene block being modified to contain an average of one or more carboxyl
20 groups; (b) a polymer comprising a polymerization reaction product of two or more mono-ethylenically unsaturated monomers in which (i) at least one of the monomers is an acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive and (ii) at least one of the monomers has carboxylic acid functionality and is present in an amount ranging from about 1 to about 15 parts by
25 weight, based on 100 parts by weight of polymer (b); polymer (b) does not comprise a nitrogen-containing monomer; and applying an adhesive to the primed substrate. In some preferred embodiments, the substrate is a low energy substrate. As used herein, "low energy substrate" refers to a substrate having a critical surface tension of wetting no greater than about 35 dynes/cm. Examples include polyolefin
30 polymers such as polyethylene and polypropylene.

The invention provides polymer blends that exhibit good adhesion to both low energy surfaces (e.g., polyolefins such as polyethylene and polypropylene), as well as higher energy surfaces (i.e., having surface energies greater than 35 dynes/cm such as metal and glass). The blends are useful as primers (e.g., for paints and coatings), adhesives (e.g., for use as tie layers), pressure sensitive adhesives, inks, and paints.

Detailed Description of the Invention

The invention features blends comprising (a) a modified block copolymer and (b) a polymer, as set forth in the Summary of the Invention section.

The block copolymer comprises one or more polystyrene blocks. If one or two polystyrene blocks are present, the block copolymer can be designated as an AB block copolymer (containing one polystyrene block) and an ABA block copolymer (containing two polystyrene blocks), "A" designating polystyrene and "B" designating polydiene or hydrogenated polydiene.

Examples of a polydiene block or hydrogenated polydiene block include, e.g., a polybutadiene, polyisoprene, ethylene/butylene, or ethylene/propylene block. The term "polydiene" refers to repeating units of a diene monomer. The hydrogenated polydiene block preferably has a residual unsaturation of less than 10%, more preferably less than 5%, based on the original amount of ethylenic unsaturation of the polydiene block. Examples of compounds which may be reacted with the polydiene block or the hydrogenated polydiene block to provide the substituent carboxyl groups include carboxylic acids and anhydrides (e.g., maleic acid and maleic anhydride).

A particularly preferred block copolymer is a maleated styrene-ethylene/butylene-styrene block copolymer. The term "maleated" means that the polydiene or hydrogenated polydiene block is modified, for example, with maleic acid or maleic anhydride so that the polydiene or hydrogenated polydiene block contains an average of one or more carboxyl groups. An example of a preferred copolymer is a styrene-ethylene/butylene-styrene triblock copolymer containing 2% by weight succinic anhydride (the source of the carboxyl groups) (commercially

available from Shell Chemical Company, Houston, TX, under the trade designation "Kraton FG-1901X"). "Kraton FG-1901X" has a tensile strength of about 5000 psi, a percent elongation of about 500, a Shore A hardness of about 75, a specific gravity of about 0.91, and a Brookfield viscosity of about 1250 cps at 77°F (25°C).

5 Block copolymer (a) has a ratio, by weight, of polystyrene block to polydiene block or hydrogenated polydiene block typically ranging from about 5:95 to 95:5, preferably 10:90 to 50:50.

 Polymer (b) comprises a polymerization reaction product of two or more mono-ethylenically unsaturated monomers in which (i) at least one of the monomers
10 is an acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive and (ii) at least one of the monomers has carboxylic acid functionality and is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b); and polymer (b) does not comprise a nitrogen-containing monomer.

15 The non-tertiary alcohol preferably includes methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-pentanol, 2-pentanol, 3-pentanol, 2-methyl-1-butanol, 1-methyl-1-butanol, 1-methyl-1-pentanol, 2-methyl-1-pentanol, 3-methyl-1-pentanol, 2-ethyl-1-butanol, 3,5,5-trimethyl-1-hexanol, 3-heptanol, 2-octanol, 1-decanol, or 1-dodecanol. A particularly preferred ester monomer is iso-octyl acrylate.

20 In a preferred embodiment, the homopolymer of the acrylic or methacrylic acid ester has a T_g less than 20°C. A polymeric moiety having a T_g greater than 20°C, a weight average molecular weight above 2,000, and capable of associating with one or more of the blocks of the block copolymer (e.g., a polystyryl moiety as described in Groves, U.S. Patent No. 5,143,972 entitled "Pressure-Sensitive
25 Adhesive Composition" which is hereby incorporated by reference) may be polymerized with the acrylic or methacrylic acid ester portions of the polymer. In this case, association is believed to occur between this polymeric moiety and the phenyl groups of the styrene blocks.

 Examples of monomers having carboxylic functionality include acrylic acid,
30 methacrylic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, and citraconic acid. This monomer is generally present in an amount ranging from

about 1 to about 15 parts, based on 100 parts by weight of polymer (b), preferably in an amount ranging from 1 to 10.

Polymer (b) may also contain a monomer having hydroxyl functionality, e.g., 2-hydroxy-ethyl acrylate and 2-hydroxy-ethyl methacrylate. A monomer having
5 hydroxy functionality can be present in an amount ranging from about 1 to about 10 parts by weight, based on 100 parts by weight of polymer (b), preferably 1 to 5.

Polymer (b) is not crosslinked and is preferably prepared by free radical-initiated photopolymerization or thermal polymerization of the base monomers using conventional polymerization techniques.

10 Block copolymer (a) and polymer (b), and any optional additives, may be physically blended together to form a blend of the present invention.

Block copolymer (a) is present in an amount sufficient to allow association with the substrate, particularly if the substrate is a low energy substrate. Polymer (b) is present in an amount sufficient to associate with block copolymer (a). The
15 term "association" or "associate" as used herein with respect to the interaction between a substrate and block copolymer (a) refers to the bonding or contact between the substrate and block copolymer (a) such that the substrate, particularly a low energy substrate, is made more receptive to materials such as inks; paints; and adhesives. That is, block copolymer (a), and ultimately polymer (b) create an
20 energy gradient between the substrate and a higher energy material, for example, an adhesive and/or paint, which is to be bonded to the substrate. The term "association" or "associate" as used herein with respect to polymer (b) and block copolymer (a) refers to the bonding or contact between polymer (b) and block copolymer (a) such that each interacts the other.

25 The ratio of block copolymer (a) to polymer (b) by weight preferably ranges from about 95:5 to about 5:95, more preferably from about 75:25 to about 25:75.

Examples of preferred polymer blends include (1) a blend of maleated styrene-ethylene/butylene/styrene block copolymer and iso-octyl acrylate/acrylic acid polymer; (2) a blend of maleated styrene-ethylene/butylene/styrene block
30 copolymer and iso-octyl acrylate/methacrylic acid polymer; and (3) a blend of maleated styrene-ethylene/butylene/styrene block copolymer and iso-octyl

acrylate/maleic anhydride polymer. The blend may be provided in the form of a primer and/or a paint, ink, or adhesive (e.g., a pressure sensitive adhesive) by using additives, for example, as described below.

As a primer, the polymer blend is particularly useful in the case of low energy substrates. As used herein, "low energy substrate" refers to a substrate having a critical surface tension of wetting no greater than about 35 dynes/cm. Examples include polyolefin polymers such as polyethylene and polypropylene.

The blends can be tackified by incorporating a tackifying agent, modifying the structure of the acrylate or methacrylate ester-containing polymer, or through a combination of both. Tackifiers suitable for tackifying the blends include low molecular weight hydrocarbon resins, and a- and b-pinene based resins. Many tackifiers are commercially available, and optimum selection thereof can be accomplished by one of ordinary skill in the adhesive compounding art. Representative examples of commercially available tackifiers suitable for the blends include the resins available under the trade designations "Regalrez 1018," "Regalrez 1078," and "REZ-D 2084," all of which are available from Hercules Inc., Wilmington, DE; "Escorez-143H" and "Escorez 5380," both of which are available from Exxon Corp., Houston, TX; and "Wingtack Plus," available from Goodyear Tire and Rubber Company, Akron, OH. The amount of tackifier included in the blend preferably ranges from about 20 to about 250 parts per hundred parts of the blend. In general lower concentrations of tackifier are used where the blend is in the form of a primer, whereas higher concentrations are used where the blend is in the form of a pressure sensitive adhesive.

The blends may include an anti-oxidant to inhibit oxidation of the tackifying agent and consequent loss of tackiness as the blends age. Suitable anti-oxidants are based on either (1) a hindered phenol or (2) a sulfur-containing organo-metal salt. Examples of hindered phenols include ortho-substituted or 2,5-disubstituted phenols where the substituent group or groups is a branched hydrocarbon radical having 2 to 30 carbon atoms, e.g., tertiary butyl or tertiary amyl radicals. Other hindered phenols useful in practicing the invention include para-substituted phenols where the substituent groups are OR^1 , where R^1 is methyl, ethyl, 3-substituted propionic ester,

etc. Examples of commercially available hindered phenols include those available from Ciba-Geigy Corp., Hawthorne, NY, under the trade designation "Irganox 1076" and those available from American Cyanamid Company, Wayne, NJ, under the trade designation "Cyanox LTDP." Suitable sulfur-containing organo-metal salts are the nickel derivatives of dibutyl dithiocarbamate.

The blends may further include inorganic fillers such as calcium carbonate, clay, talc, silica, and limited amounts of carbon black, as well as organic fillers such as wood flour and starch. Calcium carbonates, clays, and talcs are most commonly used. The blends can also be colored by including dry pigments or color concentrates (usually polystyrene based); coloring is often desired where the blends are in the form of paints or inks. Typical pigments include titanium dioxide and carbon black. Stabilizers such as fungicides and mildewicides can be included as well.

Additives which may be included in the blends of the present invention include titanate acid esters (also known as titanates), silanes, and chlorinated polyolefins ("CPOs"). Furthermore, resins such as epoxy resins, may be blended with block copolymer (a) and polymer (b). The amounts of such additives can vary according to the blend desired. A particularly preferred additive is a titanate acid ester. Examples of titanate acid esters include ethanol, 2, 2', 2''-nitrotris-titanium (4+) salt; titanium bis(ethyl-3-oxobutanolate-O¹O³)bis 2-propanolate; a reaction product of tetraalkyltitanate with a β -diketone and an alkanolamine; and tetrabutyltitanate (1-butanol, titanium (4+) salt). Titanate acid esters are preferably present in the blend in amounts ranging from 5 to 50 parts, more preferably 5 to 30 parts, based on 100 parts by weight of a polymer blend of the present invention.

The resistance to ultraviolet light degradation of the blends can be enhanced by incorporating ultraviolet inhibitors into the blends. Typically, a 1 part per hundred (phr) loading of the ultraviolet inhibitor having the trade designation "Cyasorb IV 531" (American Cyanamid Company, Wayne, NJ) or a mixture of equal parts of ultraviolet inhibitors having the trade designations "Tinuvin 328" (Ciba-Geigy Corp., Hawthorne, NY) and "Uvinal 400" (GAF Corp., New York, NY) is sufficient to provide this enhancement. Enhanced results may be achieved

from a combination of 0.5 phr of one of the three above-mentioned ultraviolet inhibitors with a nickel chelate having one of the following trade designations: "Cyasorb UV 1084" (0.5 phr) (American Cyanamid Company, Wayne, NJ) or "NBC" (0.1 phr) (E.I. du Pont de Nemours and Company, Wilmington, DE). As
5 used herein, phr is based on the weight of block copolymer in the blend unless otherwise noted.

The above-described blends are particularly useful as primers for adhesives, e.g., pressure sensitive adhesives, thermosetting adhesives, thermoplastic adhesives, and hybrid adhesives. The term "hybrid adhesives" as used herein refers to
10 combinations of two or more different types of adhesives as well as two or more polymers suitable for forming adhesives.

Thermosetting adhesives are generally formed by addition polymerization. Examples of thermosetting adhesives include polysulfides, silicones, polyesters, polyurethanes, epoxies, anaerobic and aerobic acrylics, radiation curable polymers,
15 and vulcanizing rubbers. Thermosetting adhesives typically cure by heat, catalysts, or light or moisture activation. After curing, thermosetting adhesives are generally insoluble, i.e., the adhesive will not dissolved in an organic solvent or water and infusible, i.e., the adhesive will not flow when heated.

Pressure sensitive adhesives generally do not undergo a progressive increase
20 in viscosity after preparation, rather they are permanently in a tacky stage. Examples of pressure sensitive adhesive include those derived from polyacrylates, block copolymers as defined herein, and natural or synthetic rubber. Pressure sensitive adhesives typically possess viscoelastic properties and thus exhibit characteristics of both a viscous liquid and an elastic solid.

25 Thermoplastic adhesives are soluble and fusible materials. Examples of thermoplastic adhesives include vinyl adhesives, e.g., polyvinyl chloride, polyvinyl butyral, polyvinyl alkyl esters and ethers, and vinyl-acetate-ethylene copolymer adhesives; acrylic adhesives; hot melt adhesives; cellulosic adhesives; and asphalt adhesives. Thermoplastic adhesives may be in the form of emulsions, solutions, or
30 solids.

A primer of the present invention may be applied using a variety of techniques including dipping, spraying, brushing, rotogravure, Meier rod, and knife coating. One particularly useful application technique involves applying a primer of the present invention to the substrate and then abrading. This technique effects
5 chemical reactions induced by mechanical actions like abrading, i.e., mechano-chemistry. Suitable abrasive products include a lint-free tissue, cloth, or sandpaper. When sandpaper is used, it is preferably wet or dry and 50% of the abrasive grit size preferably ranges from 100 to 2 microns. When pressure sensitive adhesives are being bonded to a substrate, preferably the abrasive grit size ranges from 8 to 2
10 microns, most preferably from 5.5 to 2.0 microns. When structural adhesives, i.e., epoxies and polyurethanes, are being bonded to a substrate, preferably the abrasive grit size ranges from 100 to 50 microns.

The following non-limiting examples further illustrate the present invention. All percentages are in percentage by weight unless indicated otherwise.

15

EXAMPLES

TEST METHODS

20 FPL Process For Etching Aluminum

Aluminum specimens (typically 152.4 mm x 50.8 mm x 1.6 mm) (commercially available from Vincent Metals, Minneapolis, MN under the designation "2024-T3 Alclad") are treated according to the etching process described in H.W. Eichner, Forest Products Laboratory; Report No. 1842, April 1,
25 1954, Madison, WI, USA. Specifically, the specimens are treated as follows. Each specimen is rinsed in acetone and then allowed to air dry. Next, each specimen is degreased by soaking for 10 minutes in 75 g of Oaktite 164 (alkaline detergent) (commercially available from Oaktite Products, Inc., Berkeley Heights, NJ) per liter of distilled water. Each specimen is then rinsed for 2 minutes in tap water, followed
30 by immersion for 10 minutes at 71°C in an etching bath consisting of 1161 g of H₂SO₄, 156.8 g of Na₂Cr₂O₇·2H₂O, 1.5 g of 2024-T3 bare aluminum alloy chips,

and enough distilled water to make 3.5 liters of solution. Following immersion in the etching solution, each specimen is rinsed for 2 minutes with tap water and dried for 10 minutes at 66°C.

5 **Static Shear**

The shear strength of primed and unprimed substrates bonded to double-coated, pressure sensitive adhesive foam tapes or pressure sensitive transfer adhesives is determined according to the following procedure.

10 An FPL-etched, 2024-T3 aluminum strip measuring 50.8 mm x 25.4 mm x 1.6 mm with a 7 mm diameter hole on center and 10 mm from one edge of the strip is prepared from the specimen described above. Likewise, similar strips of the primed and unprimed substrate, each having a thickness that does not yield at the test temperature under the testing load, are prepared.

15 A 12.7 mm wide pressure sensitive adhesive tape carried on a release liner is adhered to the solid end of the aluminum strip (i.e., the end opposite the end with the hole) and trimmed to a length of 25.4 mm. The liner is then removed and the solid end of the substrate strip adhered to the exposed adhesive surface. The resulting specimen is placed in a horizontal position and rolled down with a 2.4 kg roller to insure intimate contact between the surfaces. After dwelling at room
20 temperature for 24 hours the specimen is placed in an air circulating oven preheated to 80°C. After 15 minutes, a 1 kg weight is hung from the specimen. The specimen is tilted 2° from the vertical in order to negate any peel forces. The time it takes for the weight to fall (in minutes) is the "static shear value". If no failure occurs after 6,000 minutes, the test is discontinued.

25

90° Peel Adhesion - Pressure Sensitive Adhesive

Peel adhesions (N/100 mm) of double-coated pressure sensitive foam tapes to various primed and unprimed substrates are determined in the following manner.

30 The matted side of a 114 mm x 15.9 mm x 0.13 mm piece of aluminum foil (commercially available from Lawrence Fredrick Company, Greenwood, IL, under the trade designation "1145-0-SB") is placed on the linerless side of a foam tape

sample carried on a release liner measuring 101.6 mm x 12.5 mm x 1.1 mm. A 2.4 kg hard-rubber-covered steel roller is then passed back and forth three times over the specimen.

Next, about 50 mm of the liner is cut from the lined side of the sample, and the sample is then placed and centered near one end of a 152.4 mm x 50.8 mm x 5.1 mm plaque of the primed or unprimed substrate. A 2.4 kg hard-rubber-covered roller is again passed back and forth three times over the assembled specimen. The procedure is then repeated to laminate a second foam tape-aluminum construction to the other end of the plaque.

After dwelling for the specified length of time at ambient temperature, the specimen is placed in a 90° peel fixture (commercially available from Consultants INTL., Network, Mentor, OH, under the trade designation "PJ-90") and mounted in an Instron tensile tester (available from Instron Corp., Canton, MA). The 90° peel adhesion is measured by removing the free end of the aluminum foil-laminated foam tape at a rate of 30.5 cm per minute. The reported peel strengths (in N/100 mm) are an average of three determinations except where noted.

Cohesive Strength

The cohesive strengths of foam tapes commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation "Scotch Brand" foam tape were determined according to the procedure of the 90° peel adhesive test, except that the tapes were bonded to a 152.4 mm x 50.8 mm x 1.6 mm, FPL-Etched 2024-T3 aluminum panel and allowed to dwell for 2 hours prior to testing. The foam tapes used were foam tapes double coated with acrylic pressure sensitive adhesives (Y-4220, VHB-4205, and VHB-4950), double-coated with a styrene-butadiene rubber (SBR) pressure sensitive adhesive (VHB-4952); and 1 mm thick acrylic transfer tape (VHB-4910). All foam tapes failed by cohesive failure of the foam core. The results shown in Table A are an average of three values for each tape. These values are used as benchmarks for the semi-quantitative peel adhesion test described below.

TABLE A

Tape	Adhesive Type	Cohesive Failure (N/100 mm)
Y-4220	acrylic	438
VHB-4205	acrylic	1050
VHB-4952	SBR	658
VHB-4910	acrylic	702
VHB-4950	acrylic	877

Semi-Quantitative Peel Adhesion

The level of adhesion of primed and unprimed substrates to pressure sensitive adhesives which cannot be determined quantitatively (e.g., where the substrate is a thin and/or flexible film or a predimensioned rigid article) are determined semi-quantitatively. Sample preparation is carried out according to the 90° peel adhesion procedure except that two or more foam tapes are used and the tape-aluminum foil laminate is secured to the substrate with hand pressure or a 2.4 kg rubber-covered-steel roller. After dwelling for a specified time (typically 15 minutes), the free end of the tape-aluminum foil laminate is pulled from the substrate by hand. If cohesive failure of the foam core is not observed, a foam tape having the next lowest cohesive strength (determined with reference to Table A, above) is bonded and then removed. This procedure is repeated with successive foam tapes (with reference to Table A, above) until cohesive failure of the foam core occurs. A semi-quantitative level of adhesion of the primed substrate to the pressure sensitive adhesive of the foam tape is then determined with reference to Table A.

Pressure-Sensitive Adhesive Test Methods

Test methods used to evaluate the parameters of flexible sheet materials coated with pressure sensitive adhesive compositions according to the invention include standard industrial tests. The standard tests are described in detail in various publications of the American Society for Testing and Materials (ASTM), Philadelphia, PA and the Pressure Sensitive Tape Council (PSTC), Glenview, IL.

The standard test methods are described in detail below. The reference source of each of the standard test methods is also given.

Shear Strength

5 **Reference: ASTM:D3654-78; PSTC-7**

 The shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the amount of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure. It is measured in terms of time (in minutes)
10 required to pull a standard area of adhesive-coated sheet material from a stainless steel test panel under stress of a constant, standard load.

 The tests are conducted on adhesive coated strips applied to a stainless steel panel such that a 12.5 mm by 12.5 mm portion of each strip is in firm contact with the panel, with one end portion of the tape being free. The panel with coated strip
15 attached is held in a rack such that the panel forms an angle of 178° with the extended free end of the tape which is then tensioned by application of a force of one kilogram applied as a hanging weight from the free end of the coated strip. The 2° less than 180° is used to negate any peel forces, thereby insuring that only the
20 sheer forces are measured in an attempt to more accurately determine the holding power of the tape being tested. The time elapsed for each tape example to separate from the test panel (in minutes) is recorded as the shear strength.

180° Peel Adhesion

Reference: ASTM: D3330-78; PSTC-1 (11/76)

25 Peel adhesion is the force required to remove a coated flexible sheet material from a test panel measured at a specific angle and rate of removal. In the examples, this force is expressed in Newtons per 100 mm (N/100 mm) width of coated sheet. The measurement procedure is as follows.

 (1) A 12.5 mm width of coated sheet is applied to the horizontal surface
30 of a clean glass test plate with at least 12.7 lineal cm in firm contact. A hard rubber roller is used to apply the strip.

(2) The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 180°. The free end is attached to the adhesion tester scale.

(3) The glass test plate is clamped in the jaws of a tensile testing machine which is capable of moving the plate away from the scale at a constant rate of 2.3 meters per minute.

(4) The scale reading in Newtons is recorded as the tape is peeled from the glass surface. The data is reported as the range of numbers observed during the test.

10

Single Overlap Shear

Two substrate plaques, each measuring 51 mm x 25.4 mm x 5 mm, are cleaned twice with a heptane-saturated soft tissue and then rinsed with ethanol. After 15 minutes, the primer solution is applied to one side of each of the plaques using a cotton-tipped applicator and allowed to dry for 30 minutes. Two drops of ethyl cyanoacrylate adhesive (commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation "Pronto CA-40") are then placed on one of the primed surfaces. Next, the remaining primed substrate plaque is placed on top of the cyanoacrylate-containing plaque to form a 12.7 mm overlap joint. Finger-tight pressure is maintained over the joint for about 0.5 minutes. Three test assemblies are prepared for each measurement and allowed to cure for 72 hours prior to testing. Joint strength is measured according to an Instron tensile tester (available from Instron Corp., Canton, MA) at a crosshead speed of 1.47 mm/min.

25

90° Peel Adhesions - Thermosetting Adhesive

Peel adhesions (N/100 mm) of films of polypropylene (PP) and low density polyethylene (LDPE) bonded with thermosetting adhesives are determined in the following manner.

A film sample, 175 mm x 75 mm x 0.25 mm, was secured to a flat surface using a 0.25 mm acrylic pressure sensitive transfer adhesive (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "F9473PC"). The surface of the sample was flooded with a primer solution and evenly abraded with a piece of 80 micron grit, fabric backed abrasive (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "3M-ITE P220"). After one minute, the surface was flooded again with primer solution and abraded for an additional one minute. The film sample was washed three times each with xylene and ethanol and dried under ambient conditions for 24 hours. A 0.5 mm layer of a two-part epoxy adhesive (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "Scotch-Weld 2216 B/A") was applied to a 152.4 mm x 101.6 mm x 1.6 mm FPL-etched 2024-T3 aluminum panel. The primed side of the film was bonded to the adhesive using pressure from a light rubber-covered roller. After 72 hours, the film was slit into three 12.5 mm test specimens. The aluminum panel was placed in a 90° peel fixture (available from Consultant INTL Network, Mentor, OH) and mounted in an Instron tensile tester (available from Instron Corp., Canton, MA). The 90° peel adhesion was measured by removing the free end of the film strips at a rate of 30.5 cm per minute. A control sample was prepared in the same manner except the sample was not flooded with primer solution and the sample was abraded in the absence of a primer solution. The reported peel strengths (N/100 mm) are an average of three determinations.

Materials

IOA isooctyl acrylate

AA acrylic acid

"Tyzor TE" a triethanolamine chelate of titanate acid, 80% solids in isopropanol.

(ethanol, 2, 2', 2''-nitrilotris-titanium (4+) salt) (commercially available from

E. I. duPont de Nemours & Company, Wilmington, Delaware under the

trade designation "Tyzor TE")

"Tyzor DC" an ethylaceto-acetate chelate of titanac acid (titanium bis(ethyl-3-oxobutanolato-O¹O³)bis 2-propanolato) (commercially available from E. I. duPont de Nemours & Company, Wilmington, Delaware under the trade designation "Tyzor DC")

- 5 "Tyzor CLA" a reaction product of tetraalkyltitanate with a β -diketone and an alkanolamine, 77% solids in isopropanol (commercially available from E. I. duPont de Nemours & Company, Wilmington, Delaware under the trade designation "Tyzor CLA")

"Tyzor TBT" tetrabutyltitanate (1-butanol,titanium (4+) salt) (commercially
10 available from E. I. duPont de Nemours & Company, Wilmington, Delaware under the trade designation "Tyzor TBT")

PSM 2-polystyrylethyl methacrylate (weight average molecular weight of about 10,000 g/mol, prepared according to U.S. Patent No. 4,554,324; 52% solids in cyclohexane)

15

Preparation of Primer Composition (1)

A 25% solution of primer composition (1) was prepared by dissolving 25.0g of styrene-ethylene/butylene-styrene elastomer containing 2% bound succinic anhydride (commercially available from Shell Chemical Company, Houston, TX,
20 under the trade designation "Kraton FG-1901X") and 0.25g of an antioxidant (commercially available from Ciba Geigy Corp., Hawthorne, NY, under the trade designation "Irganox 1076") in 75.0g of a solvent mixture of cyclohexane, xylene, and ethanol in a weight ratio of 5.5:3.5:1.0.

25 Preparation of Primer Composition (2)

A copolymer of iso-octyl acrylate and acrylic acid in a weight ratio of 95:5 was prepared as follows:

47.5 g IOA, 2.5 g AA, 0.1 azobisisobutyronitrile (commercially available from E. I. du Pont de Nemours and Company, Wilmington, DE, under the trade
30 designation "VAZO-64"), 52.5 g ethyl acetate, 9.0 g methyl isoamyl ketone and 13.5 g xylene were added to a 237 ml narrow-mouthed bottle. The solution was

purged with dry argon for three minutes. The sealed bottle was tumbled in a rotating water bath at 55°C for 24 hours. The percentage of conversion was determined to be greater than 99% by infrared spectrophotometric analysis. The solution contained 39.87% solids and had a viscosity of about 7200 cps and a measured inherent viscosity of about 0.78 dl/g.

Preparation of Primer Solutions

The following illustrates the preparation of a typical primer solution of this invention: a mixture of primer composition (1) and primer composition (2) in a 1:3 weight ratio at a total solids concentration of about 3.0% was prepared by dissolving 1.0 g of primer composition (1) and 1.9 g of primer composition (2) and 0.25g of a titanate ester or chelate, if present, as indicated below, in about 30.4g of a solvent mixture cyclohexane, xylene and ethanol in a weight ratio of 5.5:3.5:1.0.

Examples 1-7

A number of about 3.5% primer solutions of this invention were prepared by blending in a 1:3 weight ratio of primer composition (1) to acrylic polymers of primer composition (2) as shown below.

Example	Primer Composition (2)
1	IOA/AA (95/5)
2	IOA/AA (90/10) + TE
3	IOA/AA (95/5) + TE
4	IOA/AA (95/5) + CLA
5	IOA/AA (95/5) + DC
6	IOA/AA (95/5) + TBT
7	IOA/PSM/AA (90/7/3) + TE

The primer solutions were applied by brush to 152 mm x 51 mm x 5 mm plaques of low density polyethylene (LDPE), polypropylene (PP) (both available from Precision Punch and Plastics, Minneapolis, MN), and a thermoplastic polyolefin (TPO) (available from Himont USA, Inc., Lansing, MI, under the trade designation "ETA 3163"). After 10 minutes, aluminum foil-laminated foam pressure sensitive adhesive tape samples (1 mm thick acrylic pressure sensitive adhesive foam tape available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation "VHB-4205") were bonded to the primed areas as described in the test method for 90° peel adhesion. After one hour, 90° peel values were determined. Each value reported in Table I is an average of three determinations. Control peel values were also determined for unprimed plaques.

Table I

Examples	90° Peel Values (N/100 mm)		
	LDPE	PP	TPO
Control	26.0	26.0	17.5
1	140	280	263
2	140	280	701*
3	140	280	684*
4	123	316	684*
5	123	105	684*
6	88	123	684*
7	175	403	491

* foam failure

From the results of Table I it is clear that the surfaces of low energy polymers can be remarkably changed by treatment with the primer solutions of this invention, in order to improve their adhesion to acrylic pressure sensitive adhesives.

Example 8

Primer composition (1) and primer composition (2), IOA/AA of Example 1 were diluted to 3% polymer solids with a solvent blend of cyclohexane, xylene, and ethanol in a weight ratio of 5.5:3.5:1.0 and applied by brush to PP and LDPE test plaques. Peel values were determined and are compared to Example 1.

Table II

	Peel Values N/100 mm	
	LDPE	PP
Primer Comp. (1)	88	88
Primer Comp. (2) of Example 1	53	158
Example 1	140	280

The results demonstrate that while the individual blend components, when used alone, do not perform well as primers, high peel adhesions can be obtained when these components are blended together in accordance with the present invention.

Example 9

Primer composition (1) and primer composition (2) of Example 3 were mixed in weight ratios of 1:3, 1:1, and 3:1, diluted to 3% solids with a solvent mixture of cyclohexane, xylene, and ethanol in a weight ratio of 5.5:3.5:1.0 and brushed on test plaques of TPO. After 10 minutes, aluminum foil foam tape (commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation "VHB-4205") was bonded to the primed samples. After one hour peel values were determined and are shown in Table III.

Table III

Primer Composition (1) to Primer Composition (2) Ratio	Peel Values (N/100 mm)
1:3	684*
1:1	491
3:1	474

* Foam failure

The results illustrate that a wide variety of block copolymer/acrylate ester
5 polymer ratios yield effective primer compositions for low energy surfaces.

Example 10

The primer solutions of Example 3 and 4 were applied to PP and LDPE test
plaques with a lintless tissue (commercially available from Kimberly-Clark Corp.,
10 Roswell, GA, under the trade designation "Kimwipe"). After 10 minutes, 1 mm
thick acrylic transfer pressure-sensitive adhesive aluminum foil-laminated foam
tapes (commercially available from Minnesota Mining and Manufacturing Company,
St. Paul, MN, under the trade designation "VHB-4205" and VHB-4910") were
bonded to the primed samples. After one hour, the 90° peel values were determined
15 and are recorded in Table IV.

TABLE IV

Primer Solutions	Peel Values (N/100 mm)	
	PP	LDPE
Unprimed		
"VHB-4205"	26	26
"VHB- (Jim what # goes here)"	52	66
"VHB-4952"	298	210
Example 3		
"VHB-4205"	298	526
"VHB-4910"	228	281
"VHB-4952"	439	526
Example 4		
"VHB-4205"	333	614
"VHB-4910"	228	351
"VHB-4952"	439	439

From the results of Table IV it is apparent that the primer solutions of the present invention improve peel adhesion of both acrylic and styrene-butadiene rubber (SBR) pressure sensitive adhesives to substrates of low surface energy.

Example 11

About 110 g of the 3.5% primer solution of Example 3 was modified by the addition of 0.5 g of epoxy resin (commercially available from Shell Chemical Company, Houston, TX, under the trade designation "Epon 828"), 3.9 g of chlorinated polypropylene (commercially available from Eastman Chemical Company, Kingsport, TN, under the trade designation "CP 3430") and 0.5 g of silane coupling agent (commercially available from OSi Specialties, Danbury, CT, under the trade designation "Silquest A 186"). About 25 g of this solution was diluted to 1% solids by the addition of 109 g of a solvent mixture of 5.5 parts

cyclohexane, 3.5 parts xylene and 1.0 parts ethanol. This primer solution was brushed on test plaques of glass, aluminum and stainless steel. After 10 minutes, aluminum foil-laminated foam tapes (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designations "VHB-4205", "VHB-4910", and "VHB-4952") were bonded to the primed samples. After 72 hours, 90° peel values were determined; the results are recorded in Table V.

Comparative Example 11

The procedure of Example 11 was followed except that the glass, aluminum and stainless steel test plaques were primed with a formulated, commercially available chlorinated polypropylene primer (available from Norton Performance Plastics, Granville, NY, under the trade designation "Tite-R-Bond-2684").

Table V

	Peel Values (N/100 mm)		
	Glass	Al	S.S.
Unprimed			
"VHB-4205"	387	684*	315
"VHB-4910"	263	140	210
"VHB-4952"	386	386	351
Example 11			
"VHB-4205"	684*	684*	439
"VHB-4910"	631	281	316
"VHB-4952"	614	456	526
Comparative Example 11			
"VHB-4205"	32	351	35
"VHB-4910"	26	351	17
"VHB-4952"	456	491	26

* foam failure

Table V clearly shows that the primer solution of this invention improves the adhesion of both acrylic and SBR pressure sensitive adhesives to polar substrates of high surface energy compared to unprimed substrates and the primer solution of Comparative Example 12.

5

Example 12

The primer solution of Example 11 was applied to LDPE and PP test plaques with a lintless tissue (available from Kimberly-Clark Corp., Roswell, GA under the trade designation "Kimwipe"). After 10 minutes, aluminum foil-laminated
10 foam tapes (available from Minnesota, Mining and Manufacturing Company, St. Paul, MN under the trade designations "VHB-4205", "VHB-4910", and "VHB-4952") were bonded to the primed samples. After one hour the peel values were determined and the results are recorded in Table VI.

15 Comparative Example 12

The procedure of Example 12 was followed except that the LDPE and PP test plaques were primed with a formulated chlorinated polypropylene primer (available from Norton Performance Plastics, Granville, NY, under the trade designation "Tite-R-Bond-2684").

20

Table VI

Peel Values (N/100 mm)		
	LDPE	PP
Unprimed		
"VHB-4205"	26	26
"VHB-4910"	26	52
"VHB-4952"	210	298
Example 12		
"VHB-4205"	702*	702*
"VHB-4910"	596	439
"VHB-4952"	667	491
Comparative Example 12		
"VHB-4205"	298	473
"VHB-4910"	140	351
"VHB-4952"	351	403

* foam failure

The results of Table VI demonstrate that a primer solution of the present invention improves adhesion of both acrylic and styrene-butadiene rubber pressure-sensitive adhesives to substrates of low surface energy.

Example 13

A 1% primer solution prepared according to Example 11 was brushed on 125 mm x 75 mm x 0.25 mm specimens of linear low density polyethylene film (LLDPE) (commercially available from Consolidated Thermoplastics Company, Schaumburg, IL). After 15 minutes, aluminum foil-laminated foam tape available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designations "VHB-4220" and "VHB-4205" were bonded to the primed samples. After one hour, semi-quantitative peel adhesions were measured by attempting to remove the foam tapes by hand. The "VHB-4220" samples could not

be removed due to cohesive failure of the foam core. This indicated peel adhesion values of at least 425 N/100 mm had been achieved.

Although excellent adhesion of the "VHB-4205" tape was observed, it could be removed from the primed LLDPE without cohesive foam failure. After 12 hours, cohesive foam failure was observed, indicating that a peel value of about 1000 N/100 mm had been achieved.

Comparative Example 13

The procedure of Example 17 was followed except that a commercially available chlorinated polypropylene primer (available from Norton Performance Plastics, Granville, NY, under the trade designation "Tite-R-Bond-2684") was brushed on the LLDPE specimens. After 15 minutes, "VHB-4220" foam tape was bonded to the samples. After intervals of both one and twelve hours, the tape could easily be removed by hand. Peel values were estimated to be only about 90 N/100 mm or less.

Example 14

A 1% primer solution prepared according to Example 11 was brushed on two 125 mm x 75 mm x 0.25 mm specimens of LLDPE film following the procedure of Example 13. The primed specimens were then allowed to dry for 15 minutes and 24 hours, respectively. Next, the primed samples were painted with a latex semi-gloss interior enamel (available from The Glidden Company, Cleveland, OH), an interior/exterior oil-based high gloss enamel (available from Carver Tripp, Parks Corp. Somerset, MA), and an aerosol polyurethane lacquer (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation Part No - 05904). In a like manner, unprimed specimens of LLDPE film were also painted. After drying under ambient conditions for 24 hours, 125 mm x 75 mm x 0.25 mm samples of filament tape (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "Scotch Brand 898") were firmly bonded to each painted surface (primed and unprimed). After 15 minutes, the tape was quickly removed from each specimen.

Complete delamination of all paints to the unprimed LLDPE films was observed. No delamination of paint was observed from any of the primed LLDPE surface.

Comparative Example 14

5 The procedure of Example 14 was followed except that a commercially available chlorinated polypropylene primer (available from Norton Performance Plastics, Granville, NY, under the trade designation "Tite-R-Bond-2684") was brushed on LLDPE specimens. The primed specimens were painted and tested as described in Example 18. Complete delamination of all paints to the primed film
10 was observed.

Example 15

To 10 g of a 3% primer solution prepared according to Example 11 was added 1 g of titanium dioxide dispersion (available from Hüls America Inc.,
15 Piscataway, NJ, under the trade designation "GPD 82-0082"). Likewise, 1 g of carbon black dispersion (available from Borden Chemical Company, Cincinnati, OH under the trade designation "Codispersion 31L62") was added to another 10 g of the same primer solution. After mixing, both pigmented solutions were brushed on untreated LLDPE film and allowed to dry under at ambient condition for 24 hours.
20 The peel adhesions of the pigmented coatings to LLDPE film was determined by firmly bonding filament tape (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "Scotch Brand 898") to the coated surfaces in the manner previously described in Example 18. No delamination of either coating was observed when the tape was rapidly removed.
25 This example demonstrates that compositions according to the invention can be utilized to prepare coatings, inks, and paints that adhere well to low energy polymer surfaces.

Example 16

A 1% primer solution prepared according to Example 11 was brushed on 50.8 mm x 24.4 mm x 5.1 mm test plaques of thermoplastic olefin (TPO) (commercially available Himont USA Inc., Lansing, MI, under the trade designation "ETA 3163") and tested for static shear to FPL etched aluminum (available from Vincent Metals, Minneapolis, MN, under the designation "2024-T3") at 80°C under a 1.0 kg load utilizing foam tape (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "VHB-4210"). Unprimed thermoplastic olefin (TPO) specimens were also tested. The results are reported in Table VIII.

Table VIII

Primer	Static Shear Value (min.)
Control	300
Example 15	10,000 +

The results in Table VIII demonstrate that the primer solutions of the invention improve the high temperature holding power of an acrylic pressure sensitive adhesive to substrates of low surface energy.

Example 17

A 3% primer solution prepared according to Example 11 was brushed on both sides of a 150 mm x 150 mm x 0.10 mm specimen of clear, flexible polyvinyl chloride (PVC) film (available from Wiman Plastic Div., St. Cloud, Minnesota) and a 150 mm x 150 mm x 0.35 mm specimen of unpigmented, opaque thermoplastic olefin (TPO) film (available from Himont USA Inc., Lansing, MI under the trade designation "HIFAX CA10A") and allowed to dry for 30 minutes. A 0.25 mm acrylic pressure sensitive transfer adhesive carried on a removable liner (available from Minnesota Mining and Manufacturing Company, St. Paul, MN under the trade designation "F9473 PC") was laminated to one side of each of the film with a

2.4 kg hard-rubber roller. Likewise, 126 mm x 12.5 mm of the same adhesive was laminated to 130 mm x 15.9 mm x 0.13 mm strips of aluminum foil with a 2.4 kg hard-rubber roller.

The peel values of the transfer adhesive to the primed tape backings were then determined by laminating a 150 mm x 51 mm sample of each transfer tape/backing construction to 152 mm x 51 mm x 1.6 mm FPL etched aluminum plates (available from Vincent Metals, Minneapolis, MN, under the designation "2024-T3") with a 2.4 kg rubber roller. About 75 mm of liner was removed from the aluminum foil laminated transfer adhesive samples and bonded to each of the tape samples on the aluminum plate in a manner such that two test samples for each tape were prepared. The resulting samples had the following constructions: aluminum plate/transfer adhesive/primed backing (both sides)/transfer adhesive/aluminum foil. Unprimed control samples were prepared in a similar manner. The peel values are reported in Table IX.

Table IX

Peel Values (N/100 mm)	
Unprimed	
PVC	175
TPO	7
Primed	
PVC	702*
TPO	702*

* adhesive and film failure.

The example illustrates that pressure sensitive adhesive tapes having holding power to backing equivalent to the cohesive strength of the adhesive or the tensile or yield strength of the backing can be prepared.

Example 18

Plaques measuring 51 mm x 25.4 mm x 5 mm of polypropylene (PP) and high density polyethylene (HDPE) (available from Precision Punch & Plastics, Minneapolis, MN) were cleaned with heptane and rinsed with ethanol. After 15

minutes a 1% primer solution prepared according to Example 11 was applied to one side of each of the plaques using a cotton-tipped applicator. The primed plaques were then bonded together with ethyl cyanoacrylate adhesive and the overlap joint strengths determined. The results are reported in Table X.

5

Table X

Substrate	Overlap Joint Strength (N/mm ²)
HDPE	2.1
PP	7.0

This example illustrates that the primer solutions of the invention initiate the polymerization of ethyl cyanoacrylate adhesives to give high bond strengths between substrates of low surface energy.

10

Pressure Sensitive Adhesives

Example 19

This example illustrates one preferred blend according to the invention useful as a pressure sensitive adhesive.

15

The following ingredients in the amounts shown were introduced into a one liter jar.

Ingredient	Amount (g)
Maleated, Styrene-ethylene/butylene-styrene elastomer ("Kraton FG 1901X," Shell Chemical Company)	100
Tackifier ("Regalrez 1018," Hercules Inc.)	75
Tackifier ("Rez-D 2084," Hercules Inc.)	75
Tackifier ("Regalrez 1078," Hercules Inc.)	25
Antioxidant ("Irganox 1076," Ciba-Geigy Corp.)	1
Antioxidant ("Cyanox LTDP," American Cyanamid Company)	1
Ultraviolet inhibitor ("Tinuvin 328," Ciba-Geigy Corp.)	0.3
Ultraviolet inhibitor ("Uvinal 400," GAF Corp.)	0.3
Toluene	323
Ethanol	16.5

The jar was shaken until the ingredients dissolved to give a solution containing about 45% total solids and a viscosity of about 1300 cps (as measured by a Brookfield viscometer, Model HAT, Spindle No. 4, Speed 50 rpm). The solution is referred to herein as the "block copolymer."

43.3 g of the block copolymer was introduced into a 118 ml jar along with 26.2 g of an iso-octyl acrylate/2-polystyrylethyl methacrylate/acrylic acid (IOA/PSM/AA) polymer prepared according to Example 7, except no "Tyzor TE" was added. The blend was stirred vigorously until it was homogeneous. The jar was capped and heated at 65°C for about one hour. The blend was then stirred vigorously and allowed to stand overnight. The blend contained 65% by weight of the block copolymer and 35% by weight of the IOA/PSM/AA polymer. After mild agitation, the blend was coated onto oriented polyethylene terephthalate film having 0.025 mm thickness by means of a laboratory 152 mm knife coater at a knife setting of about 0.25 mm. The coated film was air dried at 95°C for 15 minutes to give an average coating weight of about 6.0 mg/cm². Samples were prepared according to test methods previously described and tested for peel adhesion to glass, low density

polyethylene (LDPE), polypropylene (PP), and stainless steel (SS) and shear strength. The results are shown in Table XI.

Table XI

5

Adhesive	Peel Value (N/100 mm)				Shear (min.)
	Glass	LDPE	PP	SS	
Example 19	59.8	129	66	63.5	130

The results of Table XI demonstrate that useful pressure sensitive adhesives can be prepared from blends according to the invention.

10 Example 24

A blend was prepared by combining 15 g of the block copolymer solution described in Example 1 and 30 g of the acrylate ester polymer described in Example 1. The blend was combined with 1 g of epoxy resin (available from Shell Chemical Company, Houston, TX, under the trade designation "Epon 828"), 3.0 g of
 15 chlorinated polypropylene (available from Eastman Chemical Company, Kingsport, TN, under the trade designation "CP 343-3"), 2.5 g of silane coupling agent (available from OSi Specialties, Danbury, CT, under the trade designation "Silquest A 186"), 4 g of triethanolamine titanate (available from E.I. du Pont de Nemours & Company, Wilmington, DE, under the trade designation "Tyzor TE"), and 99 g of a
 20 solvent mixture of cyclohexane, xylene, and ethanol in a weight ratio of 5.5:3.5:1.0 to prepare an about 18% solution.

This solution was cast onto the non-matted side of three 152.4 mm x 24.5 mm x 1.3 mm aluminum strips (available from Lawrence Fredrick Company, Greenwood, IL). A 0.25 mm thick coating of the solution dried to form about a
 25 0.037 mm thick coating of adhesive on each strip.

A 3% primer solution prepared as described in Example 11 was brushed onto three 152.4 mm x 24.5 mm x 2.5 mm plaques of thermoplastic olefin (TPO) (available from Himont USA, Inc., Lansing, MI under the trade designation "ETA 3095") and allowed to dry. The adhesive-coated aluminum strips were laminated to

about 137 mm of the primed TPO plaques at a temperature of 200°C for 30, and 45 seconds, respectively, under low pressure. Peel values were determined to be 193 N/100 mm, and 246 N/100 mm, respectively.

This example illustrates the utility of the compositions of this invention as
 5 adhesive tie layers for laminating dissimilar materials together.

Example 25

A construction using a thermosetting adhesive was prepared as described
 under 90° Peel Adhesion - Thermosetting Adhesive test method. A 5% solution as
 10 set forth in Table XII was used.

Table XII

Component	Amount (g)
solvent mixture of cyclohexane, xylene, and ethanol in a weight ratio of 5.5:3.5:10	30
styrene block copolymer (available from Shell Chemical Company, Houston, TX under the trade designation "FG 1901X")	0.23
chlorinated polypropylene (available from Eastman Chemical Company, Kingsport, TN under the trade designation "CP 343-3")	0.92
epoxy resin (available from Shell Chemical Company, Houston, TX, under the trade designation "Epon 828")	0.15
epoxy silane coupling agent (available from OSi Specialties Inc., Danbury, CT, under the trade designation "Silquest A 186")	0.15
iso-octyl acrylate/acrylic acid in a weight ratio of 95:5 (40% solids)	1.8
triethanolamine titanate (available from E.I. du Pont de Nemours & Company, Wilmington, DE, under the trade designation "Tyzor TE")	0.07

The surface of the sample was initially flooded with about 1.5 ml of the 5% solution and abraded according to the test method described above. A control sample was prepared by abrading the sample in the absence of a primer solution. The results are set forth in Table XIII.

5

Table XIII

Solution	90° Peel Values (N/100 mm)	
	LDPE	PP
Control	17.5	14.0
Example 25	140.0	300.0

The 90° peel values were dramatically increased by using a solution in accordance with the present invention as compared to an unprimed substrate.

10

Example 26

Thermoplastic polyolefin plaques, 51 mm x 25.4 mm x. 5 mm, (available from Himont USA, Inc., Lansing, MI, under the trade designation "ETA 3163") were cleaned twice with ethanol and allowed to dry. A 5% solution prepared according to Example 25 was brushed on one side of each of the plaques and allowed to dry for 24 hours.

15

The primed plaques were bonded with two-part epoxy adhesives (available from Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation "Scotch-Weld 2216 B/A") to form 25.4 mm x 12.7 mm overlap joint. The specimens were allowed to cure for 72 hours under a weight of 150 g. A control sample was prepared and run once without using any solution. Joint strengths (N/mm²) were measured in an Instron tensile tester (available from Instron Corp., Canton, MA) at a crosshead speed of 12.7 mm per minute. The values reported in Table XIV are an average of three determinations for Example 26 and a single determination for the control sample.

20

25

Table XIV

Solution	Overlap Joint Strength (N/mm ²)
	TPO
Control	0.34
Example 26	1.65

What is claimed is:

1. A polymer blend comprising
 - (a) a modified block copolymer comprising
 - (i) a polystyrene block and
 - (ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene block being modified to contain an average of one or more carboxyl groups; and
 - (b) a polymer comprising a polymerization reaction product
 - (i) at least one acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive,
 - (ii) at least one monomer having carboxylic acid functionality which is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b); and
 - (iii) a titanate selected from the group consisting of ethanol, 2, 2', 2''-nitrilotris-titanium (4+) salt); titanium bis(ethyl-3-oxobutanolato-O¹O³)bis 2-propanolato; a reaction product of tetraalkyltitanate with a β -diketone and an alkanolamine; and tetrabutyltitanate (1-butanol, titanium (4+) salt).
2. A blend of claim 1 wherein a homopolymer of said ester has a Tg less than 20°C.
3. A blend of claim 1 wherein said ester comprises iso-octyl acrylate.
4. A blend of claim 1 wherein said monomer having carboxylic functionality is selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, and citraconic acid.

5. A blend of claim 1 wherein a polymeric moiety capable of associating with one or more of the blocks of said block copolymer (a) is polymerized with said acrylic or methacrylic acid ester of said polymer (b), said polymeric moiety having a Tg greater than 20°C and a weight average molecular weight above 2,000.

6. A blend of claim 1 wherein said block copolymer (a) is present in an amount sufficient to associate with the substrate.

7. A blend of claim 1 wherein said polymer (b) is present in an amount sufficient to bond to said block copolymer (a).

8. A blend of claim 5 wherein said titanate (c) is present in an amount ranging from 5 to 50 parts by weight, based on 100 parts by weight of the polymer blend.

9. A blend of claim 1 wherein said block copolymer (a) and said polymer (b) are present in a weight ratio ranging from about 95:5 to about 5:95.

10. A method of priming a substrate comprising applying to the substrate a blend comprising

(a) a modified block copolymer comprising

(i) a polystyrene block and

(ii) a polydiene block or a hydrogenated polydiene block, said polydiene block or hydrogenated polydiene block being modified to contain an average of one or more carboxyl groups; and

(b) a polymer comprising a polymerization reaction product of

(i) at least one acrylic or methacrylic acid ester of a non-tertiary alcohol having 1 to 14 carbon atoms, inclusive,

(ii) at least one monomer having carboxylic acid functionality which is present in an amount ranging from about 1 to about 15 parts by weight, based on 100 parts by weight of polymer (b);

- (iii) a titanate selected from the group consisting of ethanol, 2, 2',
5 2''-nitrilotris-titanium (4+) salt); titanium bis(ethyl-3-oxobutanolato-O¹O³)bis 2-propanolato; a reaction product of tetraalkyltitanate with a β -diketone and an alkanolamine; and tetrabutyltitanate (1-butanol, titanium (4+) salt).

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/06197

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L53/02 C08L33/06 B05D7/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L B05D C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,95 19393 (MINNESOTA MINING & MFG) 20 July 1995 see example 24 -----	1-9

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 August 1996

Date of mailing of the international search report

16. 09. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Schueler, D

Information on patent family members

PCT/US 96/06197

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/06531

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9519393	20-07-95	NONE	